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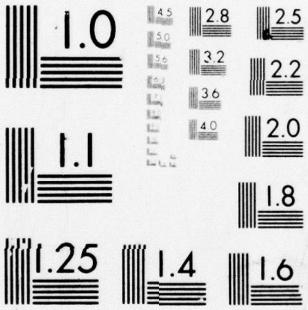
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MICROCOPY RESOLUTION TEST CHART
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Lithium Battery Session

SECONDARY BATTERIES

SECONDARY LITHIUM BATTERIES

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Introduction

In 1803, Johann Ritter discovered the concept of the storage battery;[1] by the year 1900, all our presently used secondary battery systems had been developed and a good deal of technology had evolved. It was not until the early 1960's that new concepts for secondary systems emerged. The secondary lithium battery is one such concept that appears very attractive both for military and non-military use. Although an operational room temperature secondary battery has not been demonstrated to date, it must be recalled that it took almost 30 years to commercially develop the lead-acid battery from the time of its discovery in 1859 by Gaston Planté. The problems encountered in developing a room temperature secondary lithium battery are now quite well known; some of these

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problems are discussed below and some investigations carried out at ECCM are reviewed.

Technical Discussion

General: In previous works, it was found that lithium is not generally stable in aprotic solvents but does react with such solvents as PC*[2-4] and DMF.**[5,6] It has also been found that the trace water present in these organic solvents can lead to both film formation and decreasing limiting currents.[7-11] Thus, the stability of the lithium in aprotic organic solvents has turned out to be a complex problem and a considerable amount of basic work remains to be done before practicality is achieved. It does appear, however, that the presence of SO_2 stabilizes the Li-anode in most aprotic solvents.[12]

In addition to these and other problems associated with lithium anodes, a secondary cathode has proved to be a major problem. A number of metal halides,[12-14] sulfides,[15,16] and quinones[17] are some of the cathodes that have been proposed. Secondary lithium batteries utilizing metal halide cathodes are very attractive; the energy densities are high, the materials are readily available, and they appear to be highly reversible. The major problem associated with metal halides is their high solubility. The present work was initiated in the hope that the solubility problem could be understood and, eventually, prevented. Although the present work deals with silver halides which are, energetically, borderline as cathode materials, they are representative of the class of metal halides known as soft acids; i.e., Ag^+ is a "soft-acid" in the Pearson sense[18] and is representative of the typical soft-acids such as Cu^+, Hg^+, Tl^+, Cd^{2+}, Tl^{3+}, etc. The divalent cations of Fe, Co, Ni, and Cu are, behaviorally, borderline between hard and soft.[18] Consider the cell

$$\text{Li/organic electrolyte/AgCl, Ag} \qquad (1a)$$

for which the overall cell reaction is

$$Li + \underline{AgCl} = Li^+ + Cl^- + Ag \qquad (1b)$$

Self discharge of the anode can occur if the cathode is soluble, the two major mechanisms of self discharge being

$$Li + Ag^+ = Li^+ + Ag \qquad (2)$$

and

$$Li + AgCl_2^- = Li^+ + Ag + 2Cl^- \qquad (3)$$

The major equilibria involving solubilization of the cathode are, therefore,

$$AgCl = Ag^+ + Cl^- \ (K_{s0}) \qquad (4)$$

and

$$\underline{Ag\,Cl} + Cl^- = Ag\,Cl_2^- \ (K_{s2}) \qquad (5)$$

The inability to develop a well behaved secondary lithium/metal halide battery is attributable to the large values of K_{s2}. Attempts have been made to suppress reaction (5) by the addition of a "hard-acid", such as $AlCl_3$, which very effectively removes free halide in solution by forming $AlCl_4^-$. This approach can lead to serious limitations such as deposition of Al at the anode, and inability to recharge the cathode. In the present approach, this problem is studied in terms of ion solvent interactions. By using mixed aprotic solvents, it is hoped that the Cl^- ion may be weakly stabilized in solution (rather than forming $AlCl_4^-$) and at the same time, the $AgCl_2^-$ ion is destabilized.

Experimental

The complex solubilities of AgCl, AgBr, and AgI were determined potentiometrically by titrating a halide solution with standard $AgClO_4$. A silver wire was used as the indicator electrode and the reference electrode was Ag/Ag^+ separated by a salt bridge. Tetrapropyl ammonium salts were used to maintain a constant ionic strength, usually 0.1000 M, throughout the titration. All salts were purified by the methods described by Mann[19] and the solvents were purified by fractional distillation. The titration vessels were fitted with ground glass joints and were assembled and sealed in a dry box. The emf measurements were recorded at 25±0.1°C. The stability constants and solubility constants were calculated by an iterative method.[20,21] The solvent systems studied were mixtures of propionitrile with SO_2 (PN/SO_2), propylene carbonate with tetrahydrothiophene, (PC/THT), and acetone with water, (AC/H_2O). The results are given in Table I along with some data from other investigations.

TABLE I
VALUES OF K_{s0} AND$_{s2}$ IN SEVERAL SOLVENTS AT 25°C

SOLVENT	$-\log K_{s0}$			$\log K_{s2}$		
	Cl	Br	I	Cl	Br	I
PC[a]	20.2	20.6	20.8	1.0	0.3	1.3
PC-THT (0.09 M)	12.1	12.5	13.7	1.0	0.7	0.8
PC-THT (0.56 M)	9.4	10.0	10.9	1.1	1.0	1.4
PN	15.3	16.0	17.1	1.7	1.3	1.2
PN-SO_2 (0.95 M)	11.5	12.6	14.6	-1.6	-1.5	-0.8
PN-SO_2 (3.30 M)	10.4	11.5	13.7	-2.5	-2.4	-2.3
AC	21.2	21.6	23.0	1.6	1.7	1.4
AC-H_2O (0.55 M)	19.9	20.6	22.0	1.2	1.2	1.1
AC-H_2O (3.95)	15.2	16.6	19.0	-0.6	-0.2	0.3
AC-H_2O (9.36 M)	13.4	15.0	17.8	-1.6	-1.8	-0.6
DMSO[b]	10.6	10.6	11.6	1.6	1.1	1.2
H_2O[c]	9.8	12.3	16.0	-4.4	-4.7	-4.8

a. FROM REFERENCE 22.
b. FROM REFERENCE 23.
c. FROM REFERENCE 24.

ALL OTHER DATA ARE THE PRESENT RESULTS.

Discussion

The effect of solvent composition on the various equilibria is quite large. To determine the specific effect on each ion, one can examine the individual ionic free energies of transfer, $\triangle G_t^\circ$ (ion), from water to the specific solvent s. The extrathermodynamic assumption[25] used to evaluate $\triangle G_t^\circ (Ag^+)$ is

$$\triangle AG_t^\circ(Ag^+) = (\triangle G_t^\circ (Ag^+, AgCl_2^-) + \triangle G_t^\circ(Ag^+, AgBr_2^-))/2 \qquad (6)$$

where

$$\triangle G_t^\circ(Ag^+, AgX_2^-) = 2.3RT\,(\log (K_{s2},w\;K_{s0},w/K_{s2},s \cdot K_{s0},s)) \qquad (7)$$

and

$$\triangle G_t^\circ(Ag^+, X^-) = 2.3RT \log (K_{s0},w/K_{s0},s) \qquad (8)$$

In Equations (7) and (8), X = Cl or Br. The results for the

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*PC = propylene carbonate
**DMF = dimethyl formamide

individual $\triangle G^\circ_t$(ion) values are given in Table II. It is noted that the Ag^+ ion is generally more stable in the aprotic solvent than in water while the reverse is true for the Cl^- ion. It is also seen that the anion stability increases in the aprotic solvent as the ionic radius increases. This effect is attributed to mutual polarization as discussed elsewhere.[23] The effects on Cl^- solvation appears, however, to be quite different. Addition of THT to the aprotic solvent has negligible effect on $\triangle G^\circ_t(Cl^-)$, whereas SO_2 additions significantly stabilize the Cl^- ion. This latter effect indicates the existence of an SO_2-Cl^- complex which means that SO_2 can behave, simultaneously, as a strong Lewis base and a weak Lewis acid. Bonding of the SO_2-Cl^- complex presumably occurs through the empty 3-p orbitals on the sulfur. The solvation of Cl^- with THT on the other hand occurs via interaction with the ring structure of THT and not with the S-atom. Additional work on these effects is in progress.

TABLE II
SINGLE ION FREE ENERGIES OF TRANSFER FROM WATER AT 25°C

Ion / Solvent	ΔG^0_T (ion) Ag^+	Cl^-	Br^-	$AgCl_2^-$	$AgBr^-$
MeOH	2.2	2.7	2.2	3.0	1.8
DMF	-3.1	10.0	7.2	2.1	-1.4
DMSO	-7.6	8.7	5.6	0.6	-2.6
PN	-2.0	9.5	7.0	1.2	-1.2
PN-SO_2 (0.95 M)	-2.8	5.1	3.2	1.2	-1.2
PN-SO_2 (3.30 M)	-3.0	3.8	1.9	1.2	-1.2
PC	5.3	8.6	6.0	1.5	-0.8
PC-THT (0.09 M)	-5.7	8.8	0.9	1.4	-1.4
PC-THT (0.56 M)	-9.5	9.0	1.4	1.4	-1.4

NOTE: ΔG^0_T (ION) VALUES ARE IN K CAL MOL^{-1}.

Conclusions

The addition of sulfides to the aprotic solvents is seen to display varying behavior. Both SO_2 and THT increase K_{s0} extremely rapidly even when present in small amounts. This is attributable[25] to π-bond formation between Ag^+ and the S-atom (this is in addition to the σ-bond). The interesting difference between the two systems lies in the fact that SO_2 additions to PN greatly reduce K_{s2} whereas THT additions to PC virtually has no effect on K_{s2}. It would appear, therefore, that in the presence of SO_2, the Cl^- ion is stabilized by dipolar coordination to SO_2 or by π-bonding. The dipolar coordination of Cl^- to PC and THT appears to be similar, resulting in little change in K_{s2}. This phenomenon is being investigated further to establish the site of Cl^- coordination and its nature (i.e., ionic, dipolar, covalent). The effect of H_2O additions to AC, PC,[20] and DMSO[26,27] is much less than that of the corresponding sulfides. Thus, trace amounts of water in organic solvents should have a minimal effect on a metal-halide cathode but, as discussed above, its effects on the anode are quite important.

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